

"The Halogen Hydrides as Conducting Solvents.—Part IV. Preliminary Notice." By B. D. STEELE, D. M'INTOSH, and E. H. ARCHIBALD. Communicated by SIR WILLIAM RAMSAY, K.C.B., F.R.S. Received November 29,—Read December 15, 1904.

Recent investigations have shown that the power of forming conducting solutions is manifested to a greater or less extent by a large number of inorganic and organic solvents. Some of the resulting solutions behave in a similar manner to those in water, as regards the variation with dilution of the molecular conductivity  $\mu$ , and of the average molecular weight of the dissolved substance. Others show a variation of  $\mu$  which appears to be inconsistent with Arrhenius' theory of ionic dissociation.

Conducting solutions in which the halogen hydrides and sulphuretted hydrogen act as solvents, are strikingly abnormal, and show, as has been pointed out in Parts 1 and 2,\* an enormous diminution of  $\mu$  with dilution, instead of the steady slow increase required by the theories of Arrhenius, Van't Hoff and Ostwald.

These abnormal results can, we believe, be simply explained on the assumption that the dissolved substance enters into combination with the solvent, and that the resulting compound undergoes ionic dissociation. It can be shown from the law of mass action that, if  $n$  molecules of solute combine with  $m$  molecules of the solvent to form a single molecule of the electrolyte, the concentration of the latter will be proportional to  $\nu^{-n}$ , where  $\nu^{-1} = c$  is the concentration of the original dissolved substance. But the specific conductivity  $\kappa$  is proportional to the number of ions, and this is proportional to the concentration of the electrolyte multiplied by  $\alpha$ , where  $\alpha$  is its coefficient of ionisation. Thus

$$\kappa = \alpha K c^n = \alpha K / \nu^n, \text{ if } n = 2,$$

or

$$\kappa \nu^2 = \alpha K.$$

If  $\alpha$  varies but slightly over a given range this equation becomes

$$\kappa \nu^2 = K'.$$

It is found that the whole of our results may be thus explained. In some cases  $\kappa \nu^2$  is approximately constant over a certain range of dilution; and that this approximate constancy does not hold at greater dilutions is to be assigned to the variation of  $\alpha$ , which may become greater in more dilute solutions on account of a secondary dissociation intervening.

\* 'Roy. Soc. Proc.,' vol. 73, pp. 450 and 455.

This behaviour is manifested by, amongst others, a solution of hydrocyanic acid in hydrogen chloride, which gives the following values for  $\nu$  and  $\kappa\nu^2$ .

$$\begin{array}{cccccccc} \nu = & 41.4 & 21.6 & 14.1 & 10.2 & 3.12 & 2.56 & 1.79 & 1.23 \\ \alpha K = \kappa\nu^2 = & 2.11 & 1.96 & 1.40 & 1.20 & 1.15 & 1.15 & 1.04 & 0.94 \end{array}$$

From these it will be seen that according to the foregoing explanation,  $\alpha$  increases with dilution, a variation which is that required by the ionic theory.

In the case of triethylammonium chloride dissolved in hydrogen chloride  $\alpha$  varies to a much greater extent, as the following figures show

$$\begin{array}{ccccccc} \nu = & 37.0 & 16.1 & 9.43 & 6.13 & 4.25 & 3.64 \\ \kappa\nu^2 = \alpha K = & 66.7 & 43.7 & 34.3 & 31.6 & 28.5 & 28.0 \end{array}$$

In both the foregoing cases  $n$  is found to be equal to 2, or two molecules of solute combine with the solvent to form the dissociating substance.

In other cases  $n=3$ , or three molecules combine with the solvent, as for example, acetone dissolved in hydrogen bromide, for which solution

$$\begin{array}{ccccccc} \nu = & 8.33 & 5.00 & 3.23 & 1.64 & 1.35 & 1.07 & 0.75 \\ \kappa\nu^2 = \alpha K = [7.00] & 8.50 & 8.1 & 6.3 & 5.9 & 4.9 & 3.2 \end{array}$$

Here again the increase of  $\alpha$  with dilution is clearly indicated.

For substances dissolved in water  $n = 1$  and  $K = \mu_\infty$ , and since  $\kappa\nu = \mu_\nu$  the equation  $\kappa = \alpha K\nu^n$  becomes

$$\mu_\nu = \alpha\mu_\infty, \quad \text{or} \quad \alpha = \mu_\nu/\mu_\infty,$$

and for purposes of comparison with the foregoing the corresponding numbers for  $\nu$  and  $\kappa\nu$  are given for a salt. ( $\text{Cd SO}_4$ ) dissolved in water.

$$\begin{array}{ccccccc} \nu = & 100 & 50 & 20 & 10 & 5 & 2 & 1 \\ \kappa\nu = \alpha K = & 71.8 & 61.8 & 49.6 & 42.4 & 36.2 & 29.1 & 23.8 \end{array}$$

Confirmation of these views is afforded by the results of the molecular weight determinations, which show that in many instances the molecular weight is greater than the normal, indicating that association has taken place to some extent.